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New Developments in Gasifier Refractories

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INTRODUCTION

For Integrated Gasification Combined Cycle (IGCC) systems, operational reliability depends in part upon the ability of the materials of construction to tolerate harsh, high-temperature environments for extended periods of time. The harshest conditions within an IGCC system occur inside the gasifier itself, where for slagging systems the environment includes elevated temperature and pressure, as well as the presence of corrosive slags and gases. Attempts to enhance gasifier performance by operating at higher temperatures, with higher throughputs, and/or with variable feedstocks, put additional stress on the materials exposed to the operating environment, often resulting in a corresponding decrease in their useful service life. Current generation refractory materials commonly used at the hot face of commercial slagging systems will typically last from four to 18 months, depending on the operating conditions of the specific gasifier. However, as gasification technology matures, the need for new and improved materials will increase as the time between required maintenance shutdowns, and hence the economics and reliability of operation, are defined more and more by the service life of the materials from which the system is built. To address this need for materials development, the U.S. Department of Energy's Office of Fossil Energy and the Albany Research Center are exploring ways to extend the service life of the refractory liner that contains the gasification reaction in slagging gasifiers. In this paper, we examine how refractory materials fail in the gasifier environment, and introduce a new refractory designed specifically to resist such failures. Based on laboratory exposure tests, this new refractory is predicted to significantly enhance gasifier reliability and availability through increased service life.

REFRACTORIES IN SLAGGING GASIFIERS

Refractories are a class of ceramic materials that are uniquely capable of insulating and containing harsh, high-temperature, corrosive and erosive environments. As a result of their stability, refractories are utilized in a variety of industrial processes, including the manufacturing and processing of metals, glass, chemicals, pulp and paper, and petroleum-based products. Although refractories are not typically high-profile elements in any of these industrial processes, their performance nonetheless plays a pivotal role in determining the efficiency, reliability and economics of production. In IGCC power production, as well as in other gasification-based processes, refractory materials are frequently utilized to contain the high-temperature gasification reaction and to protect the outer steel shell of the gasifier from temperature, corrosion, and wear. Typical temperatures inside slagging coal gasifiers range from 1300º to 1600º C, depending upon the melting point and viscosity characteristics of the residual ash. In addition to high temperature, the refractory lining inside a slagging gasifier must also be able to withstand a number of other challenges, including large and sometimes sudden variations in temperature; load at high temperatures; alternating oxidizing and reducing environments, wear by corrosive slags; erosion by residual particulates; and high pressures. A number of studies conducted during the 1980's at the Cool Water demonstration plant [1-5], and subsequently at other slagging gasifier facilities [6,7], indicate that because of the severity of these challenges, high-chromium-oxide refractories are the only commercially available materials that can provide an acceptable service life for this application. The refractory test program at the Cool Water project suggested that a high-chromium-oxide refractory hot face lifetime of up to 3.5 years could be expected, if gasifier operating parameters and feedstock were optimized [4]. However, more-recent experience at commercial gasifier facilities utilizing less optimal feedstocks and operating conditions indicates that actual refractory lifetimes range between 4 and 18 months. The high costs associated with replacing the refractory liner (often more than US $1,000,000 in material and lost-opportunity costs combined), and the gasifier downtime required to make the refractory change (a minimum of two to three weeks if a second gasifier is not available), make refractory liner lifetime a key issue in defining gasifier economics and reliability. A recent DOE survey of gasifier manufacturers and operators indicates that the industry believes that a gasifier availability of 85-95% for utility applications and >95% for other applications is required to move this technology forward in the marketplace [8]. This requirement translates into a minimum refractory hot-face lifetime of three years in slagging gasifier systems, or at least double that which is currently available.

REFRACTORY LOSS IN SLAGGING SYSTEMS

Refractory performance in the presence of a molten slag, such as that found in a slagging gasifier, is typically determined by any one, or combination, of the following phenomena: slag penetration into the refractory, dissolution of the refractory, physical wear of the refractory, and/or spalling of the refractory. Slag penetration occurs as the molten liquid moves into the refractory through the interconnected porosity and cracks and along grain boundaries. The ease and depth of slag penetration depends upon a number of factors, including the temperature gradient across the refractory, the viscosity of the slag, and the wettability of the refractory by the slag. Slag penetration alone may not be a detriment to refractory performance; however, if slag penetration results in detrimental chemical and/or physical changes in the refractory material, it can be the primary cause of refractory failure. Dissolution of the refractory in slagging environments occurs most often as the result of chemical attack of the matrix, which disrupts and weakens the refractory structure, allowing the coarse-grained aggregate phase to be swept away. Wear occurs as a result of the mechanical action of the slag flowing over the face of the refractory, and the rate of material loss by wear is increased when dissolution of the refractory is also an issue. Spalling may occur as the direct result of mechanical or

Figure 1. Refractory brick removed from service in commercial slagging gasifiers.

thermal stress, or as the result of the physical and chemical changes induced in the material as the result of slag penetration, or as a result of the combination of these actions. Regardless of its source, spalling will usually cause rapid and significant material loss and is therefore to be avoided whenever possible.

To understand refractory loss in slagging gasifier environments, the Albany Research Center has performed extensive *post-mortem* analyses of spent refractories from commercial gasifiers which utilize coal as the primary feedstock [9,10]. While the performance of the refractory is strongly dependent upon the operating conditions of the specific gasifier, these *post-mortem* analyses indicate that slag penetration and subsequent spalling are the two principal mechanisms of material removal in most slagging gasifiers. (Vapor penetration and attack may also be problematic in some areas of the gasifier [10]; however, this is not believed to be a major source of material loss in the gasifier as a whole.) Examples of spent refractory brick in which slag penetration and spalling are a problem can be found in Figure 1. These brick are all commercially-produced, high-chromium-oxide materials, that were removed after four to 18 months of service in commercial gasifiers. The hot face surfaces of these spent refractory brick are coated with a thin layer of solidified slag, but even so, the change in dimensions of the spent brick relative to that of a virgin brick, and the wavy surface characteristic of a spalled and/or corroded material, are indications of the large volume of material loss which occurred during service. In addition, large cracks and voids are sometimes obvious deep within the slag-penetrated regions of the brick, which indicate that even single spallation events can result in the removal of relatively large volumes of material in this environment.

Figure 2. A refractory brick removed from service in a slagging coal gasifier. The slag penetrated region, and associated cracking is apparent at the top of the brick.

A cross-sectioned sample of a single refractory brick (Figure 2) provides more information about the refractory's response to the gasifier environment. Here the depth of slag penetration into the refractory is clearly evident, as are the cracks which form parallel to the hot face within the slag-penetrated region and near the interface between the slag-penetrated and the virgin material. Because of the characteristics of the slag, and the small thermal gradient in the high-chromium-oxide materials, the slag penetrates five centimeters or more into the refractory before solidifying. The changes that occur in the microstructure and properties of the refractory as a result of slag penetration result in the initiation and growth of cracks parallel to the hot face that ultimately link up and lead to spallation and material loss. Any large and/or sudden variations in gasifier operating temperature that occur during service will exacerbate material loss by this mechanism.

Examination of the microstructural changes that occur in the refractory as a result of slag penetration indicates that the slag moves into the refractory primarily through the interconnected porosity and along the grain boundaries of the refractory matrix [9,10]. Gravimetric and other laboratory exposure tests, performed over a range of operating conditions, show that the coal slags penetrate quickly and deeply into the refractory brick. However, in spite of the extensive slag penetration, dissolution of the refractory is minimal and is limited primarily to the matrix regions. Chemical analyses of the refractory composition as a function of distance from the hot face indicate that it is the silica, alkali, and alkaline earth components of the slag that penetrate the most deeply into the refractory, whereas the Fe/FeO component concentrates at the slag-refractory interface, leading to the formation of a $Fe(Al,Cr)_2O_4$ spinel at the hot face. A difference in thermal expansion characteristics between the spinel layer and the base refractory likely leads to easy removal of the surface spinel; however, because this layer is typically quite thin (<150 µm), it is unlikely to be the cause of large-scale material removal.

STRATEGIES TO IMPROVE REFRACTORY LIFE

The combined results of laboratory exposure tests and *post-mortem* analyses of spent refractories removed from slagging gasifiers indicate that while dissolution of the refractory brick by the molten slag does result in material loss in the gasifier environment, this loss is insignificant compared to the loss of material that results from slag penetration and subsequent spalling. In this environment, changes induced in the chemical and physical properties of the refractory as a result of slag penetration result in the formation of cracks parallel to the hot face, which link up and ultimately lead to material loss. Because these cracks frequently form near the interface between the slag-penetrated and virgin material, approximately five centimeters behind the hot face, their linkage results in large-scale material removal. The key to improving the performance of refractory materials in slagging gasifier environments where spalling is a problem, therefore, appears to lie in reducing the level of slag penetration. This can be achieved in a number of ways, including changing the wetting characteristics of the slag by changing the slag chemistry, reducing the wettability of the refractory, reducing the level of interconnected porosity in the refractory, changing the pore size distribution within the refractory, and/or inducing an *in-situ* change in the refractory microstructure that effectively seals the refractory surface. Any changes made to the refractory must be effective in reducing slag penetration while retaining the other beneficial properties of the material.

At the Albany Research Center, we have designed an improved refractory material for this application by applying the last of these strategies to reduce slag penetration and attack. By adding a small amount (< 10 weight percent) of a phosphate-based material ($AlPO_4$, $CrPO_4$, etc) to the matrix of a high-chromium oxide refractory, we are able to reduce slag penetration to less than one-fifth that observed in the unmodified refractory under identical conditions in laboratory exposure tests [12-15]. The results of a laboratory cup exposure test comparing the performance of a commercial high-chromium oxide refractory with the ARC-modified material is illustrated in Figure 3. In this test, a "cup" is drilled into the refractory brick and filled with a coal ash slag removed from a commercial gasifier. The slag-filled cup is then placed in a furnace and heated to 1600ºC for 24 hours in an argon environment. Following the exposure test, the refractories are cross-sectioned and examined for evidence of slag penetration and attack. As is apparent in Figure 3, the level of slag penetration in the phosphate-modified refractory is limited to

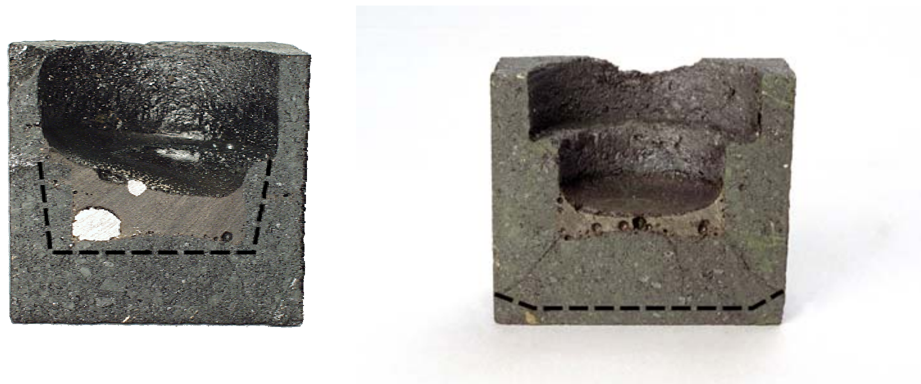

Figure 3. Albany Research Center's phosphate modified refractory (left) and conventional high-chromium-oxide refractory (right) following exposure to a coal slag at elevated temperature. The dotted lines indicate the extent of slag penetration and attack in each.

within one millimeter of the refractory-slag interface. This is compared with almost complete penetration by the slag to the bottom of the cup (a depth greater than two centimeters) in the unmodified refractory control. The mechanism for improved refractory performance in the phosphate-modified materials has not yet been fully confirmed experimentally; however, we believe that the reaction between constituents in the slag, the phosphate, and the refractory causes the slag to "freeze" much more quickly within the refractory, limiting penetration to a narrow surface region and therefore reducing the potential for large volumes of material loss by structural spalling [16]. In addition, the relatively small change in chemistry required by this process should not result in a large-scale change in the mechanical and thermal performance of the refractory product. Finally in a cooperative research and development agreement with ANH Refractories, we have proved that production of this brick can be easily scaled to a commercial setting, with the recent production of a test lot of 55 full-sized brick. Testing continues in our laboratory to fine-tune the refractory composition for optimum performance in slagging coal gasifiers, and to verify initial exposure test results utilizing more rigorous dynamic exposure tests. If as expected, these test results confirm the quality of our refractory, we expect to insert test panels of these materials in commercial gasifiers in the Spring of 2003.

SUMMARY

Future acceptance of gasification as a clean and efficient means to generate power and other products depends upon the development of gasification systems that are both more economical and more reliable to operate. For slagging gasifiers this in turn will depend in part upon the development of improved refractory materials that have a service life that is at least twice that available with current-generation high-chromium-oxide refractories.

Post-mortem analyses of spent refractories removed from commercial gasifiers indicate that rapid and deep slag penetration, combined with the resulting change in the physical and chemical properties of the slag-penetrated region, results in large volumes of material loss by structural spalling. To reduce material loss by this mechanism and significantly increase refractory life for this application, a phosphate-modified refractory has been developed at the Albany Research Center that is much more resistant to slag penetration than current generation commercial materials. Laboratory exposure tests indicate that slag penetration in the modified material is less than one fifth that of the unmodified material under identical exposure conditions. Tests continue to optimize the composition of the improved refractory for slagging gasifier applications and to confirm the results of the initial exposure studies.

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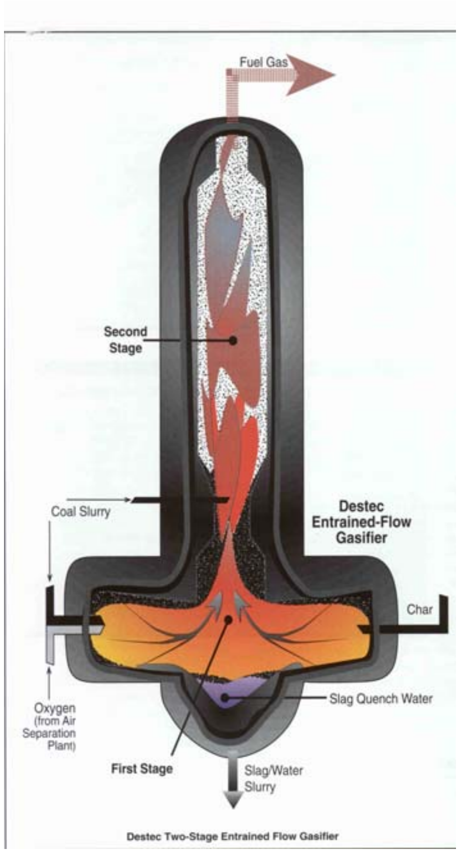
The Albany Research Center provides materials science and materials engineering solutions that help to make the Nation’s energy systems safe, efficient, and secure.

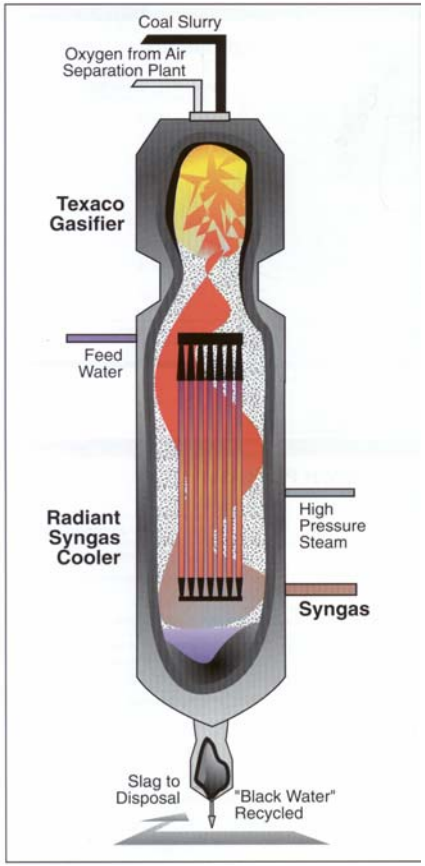
Why Refractories?

The Reliability, Availability, and Maintainability of the gasifier is directly linked to the performance of the refractory liner in slagging systems.

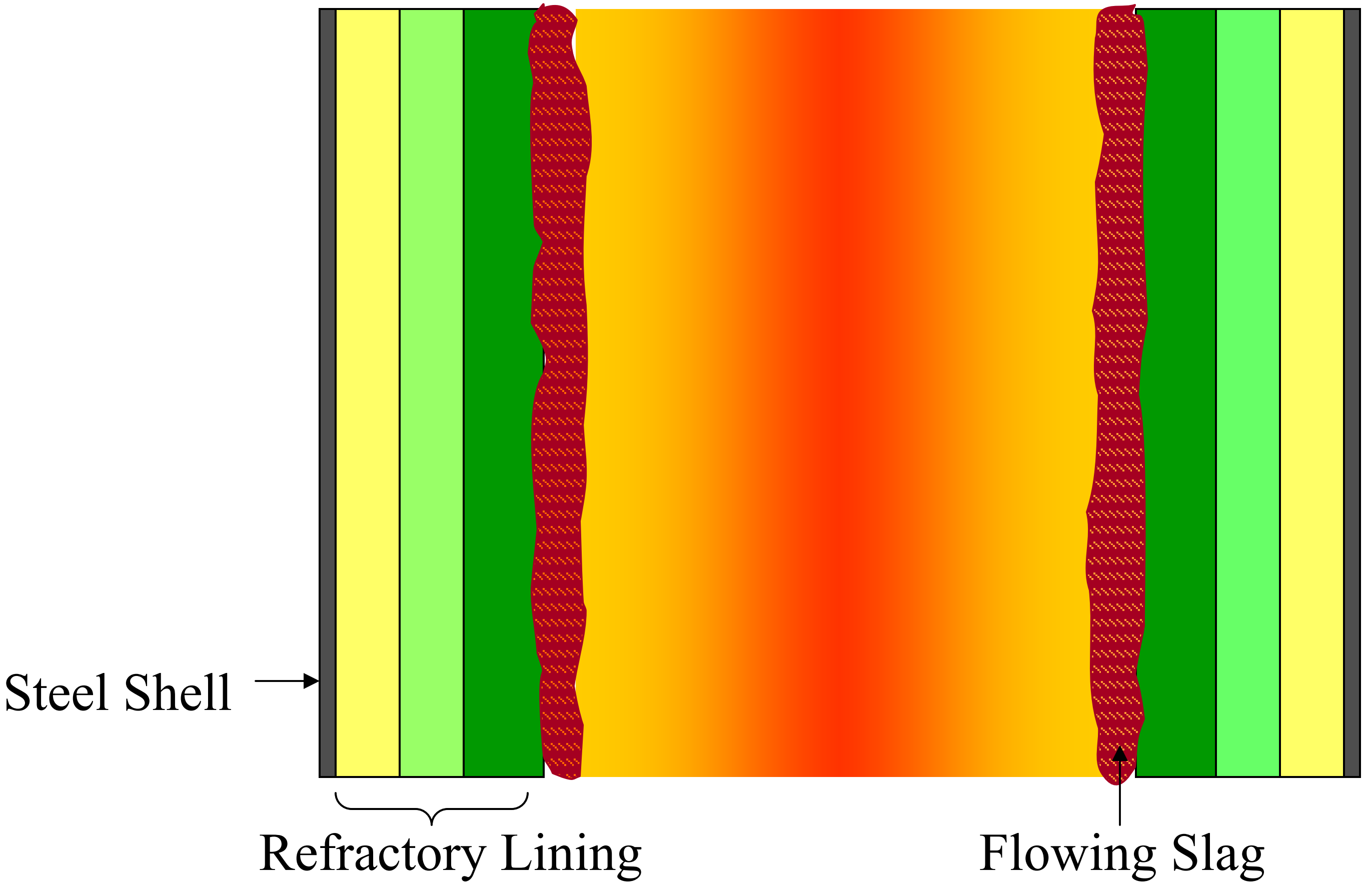
Material Challenges Inherent to Slagging Gasifier Technology



- Operating Temperatures of 1350° to 1600°C.
- Thermal Cycling.
- Alternating Reducing and Oxidizing Environment.
- Corrosive Slags of Variable Chemistry.
- Corrosive Gases.
- Pressures ≥ 400 psi.



Gasifier Containment Strategy



Current "best" refractories last 4 to 18 months, with a replacement cost of up to $1,000,000 and 2-4 weeks downtime.

Gasifier manufacturers and operators list increased refractory lifetime as one of the most important needs of the industry.

Strategies to Improve Refractory Performance in Slagging Gasifiers:

- Design a more “slag-resistant” refractory
  - Slag penetration and attack
  - Wear
- Optimize gasifier operating conditions
- Optimize refractory installation

Project Research Goals:

- Enhance gasifier reliability and economics through the development of
  - Improved refractory materials and repair techniques for longer service life.
  - Longer-life thermocouple assemblies for more reliable temperature control.

Refractories: *Post-mortem* Evaluation

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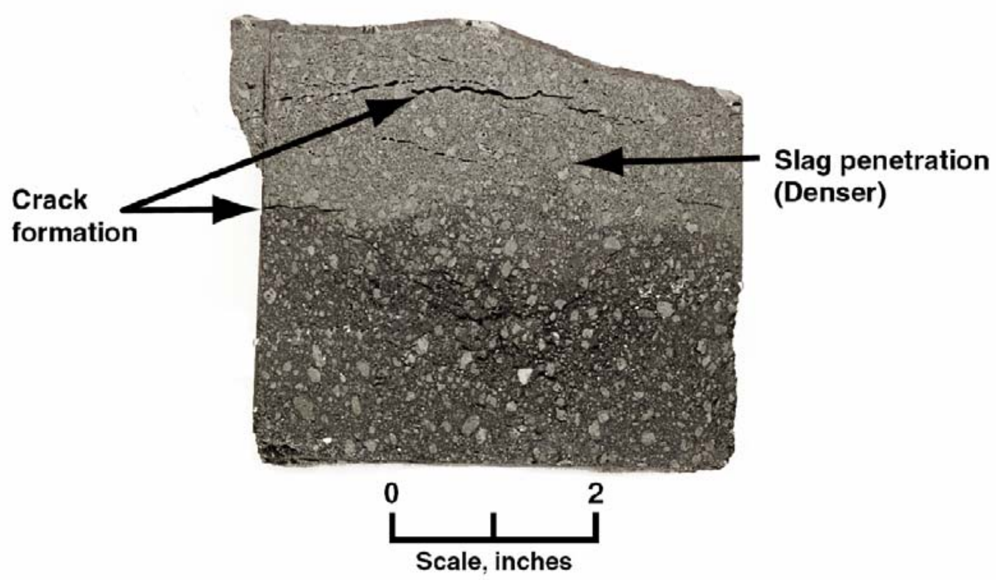
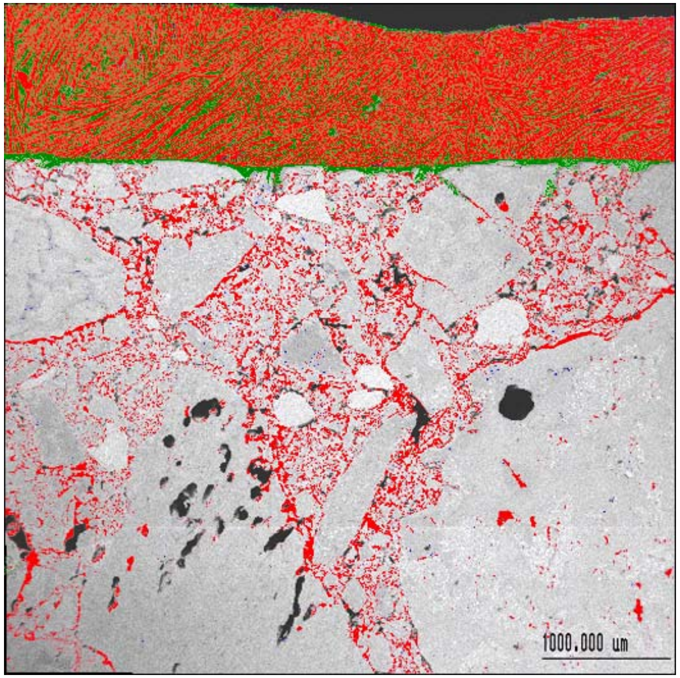
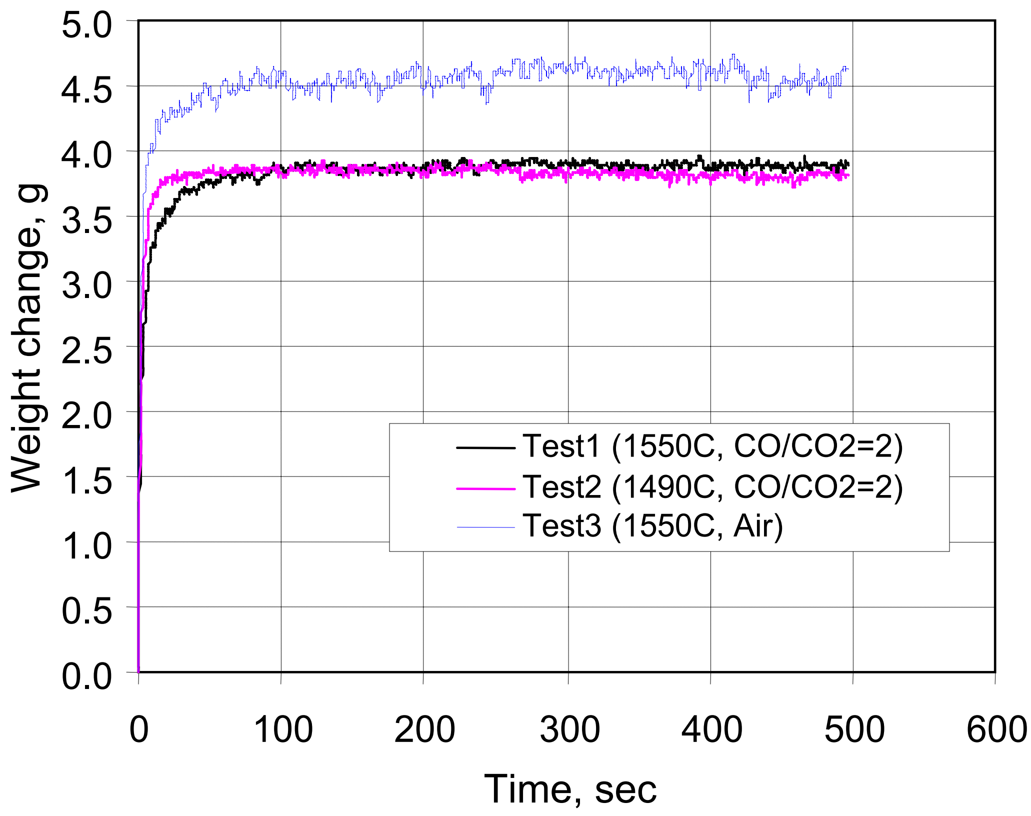
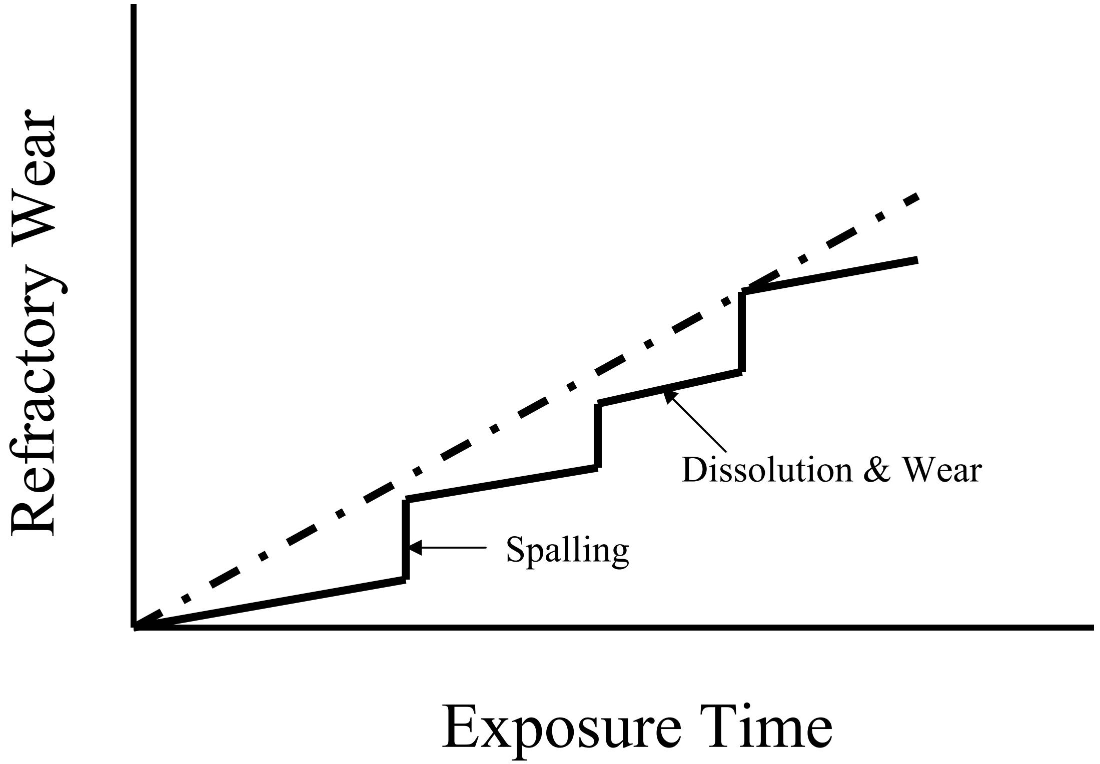




Slag Penetration is Rapid



Typical Refractory Wear in Slagging Gasifier Environments



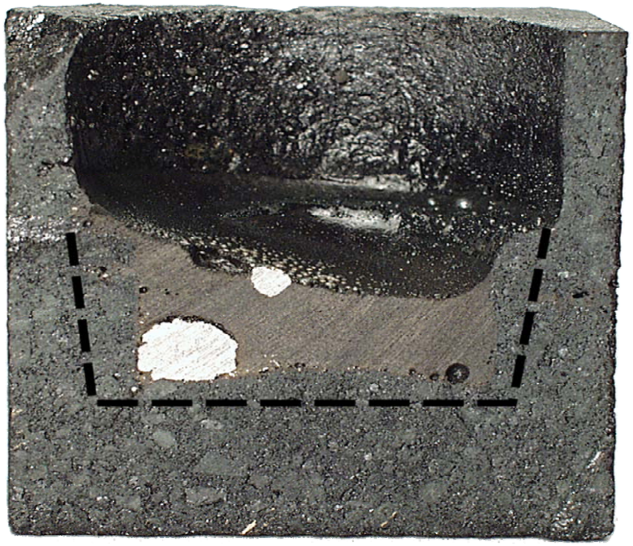
Refractories Solution:
Reduce Slag Penetration and Attack

- Reduce the volume of interconnected porosity.
- Reduce pore sizes.
- Reduce the wettability of the slag and/or the refractory.
- Induce *in-situ* microstructural changes
  - “Seal” the refractory surface.
  - Solidify the slag within the refractory more quickly.

Refractories Solution

Add phosphates ($AlPO_4$, $CrPO_4$, etc.) to the matrix to react with the slag to make the refractory more resistant to slag penetration and resultant material loss.

Refractories Solution



ARC's Improved Refractory

Current Industry Best

Refractories Solution: Optimizing Composition

Benefits of phosphate additions:

- Promote a denser refractory body.
- Enhance the bond strength between aggregates.
- Increase the viscosity of the penetrated slag.
- Increase the melting point of the penetrated slag.
- Reduce the wettability of the refractory.
- Increase the corrosion resistance.
- Increase the thermal shock resistance.

Refractories Solution: Next Step

Scale-up using commercial processing techniques to allow for expanded testing.

Refractories Solution: Next Step

Place test panels of ARC’s refractory brick in working gasifiers to verify improved performance.

Summary

A new refractory material has been developed that demonstrates improved stability in simulated gasifier environments

Improved Refractories mean:

- Reduced Gasifier Down Times.
- Reduced Operating Costs.
- Increased Reliability and Availability.